<Interface Science> Molecular Aggregates

Interface Science
- Molecular Aggregates -

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Prof
SATO, Naoki
(D Sc)

Assoc Prof
ASAMI, Koji
(D Sc)

Instr
KITA, Yasuo
(D Sc)

Instr
YOSHIDA, Hiroyuki
(D Sc)

Lecturer (pt)

Prof HIRATSUKA, Hiroshi (D Sc) Gunma University

Students

HIRAMATSU, Takaaki (D1)
YAMAGAMI, Takashi (M2)
YAMAGUCHI, Takayuki (M1)
TSUTSUMI, Jun'ya (D1)
MUROI, Kouji (M1)
HARADA, Youichiro (M2)
TSUJIKAWA, Susumu (M1)

Visitor

Prof FELDMAN, Yuri Hebrew University of Jerusalem, Israel, 10 November 2003

Scope of Research

The research at this subdivision is devoted to correlation studies on structures and properties of both natural and artificial molecular aggregates from two main standpoints: photoelectric and dielectric properties. The electronic structure of organic thin films is studied using photoemission and inverse photoemission spectrosocpies in connection with the former, and the results are applied to create novel molecular systems with characteristic electronic functions. The latter is concerned with heterogeneous structures in microcapsules, biopolymers, biological membranes and biological cells, and the nonlinearity in their dielectric properties is also studied in relation to molecular motions.

Research Activities (Year 2003)

Presentations

Electron Correlation in Molecular Films: Impact on Electronic Structure of Unoccupied States, Sato N, International WE-Heraeus Seminar (No. 306) on Energetics of Interfaces between Organic Molecules and Conductors (Bad Honnef, Germany), 20 - 22 March.

Macroscopic Current-voltage Relations of Alamethicin Ion Channels, Asami K, 25th Annual Meeting of Membrane Society of Japan (Tokyo, Japan), 8 - 9 May.

Correlation Between Polymorphism and Electronic Properties of Lithium Phthalocyanine Studied on the Basis of Electronic Structures Observed for the Unoccupied States, Sato N, Tsutsumi K, Yoshida H, Sumimoto M (Dept. Mol. Eng.), Fujimoto H (Kumamoto U.), Sakaki S (Dept. Mol. Eng.), The European Conference on Organic Electronics & Related Phenomena 2003 (Wye, U.K.), 21 - 26 September.

Dielectric Spectroscopy of Colloid and Biological cells, Asami K, 2003 Autumn Meeting of Physical Society of Japan (Okayama, Japan), 20 - 23 September.

Polymorphism and Electronic Structures of Unoccupied States in Lithium Phthalocyanine Thin Films Studied using Inverse Photoemission Spectroscopy, Sato N, Tsutsumi K, Yoshida H, Fujimoto H (Kumamoto U.), Sumimoto M (Dept. Mol. Eng.), Sakaki S (Dept. Mol. Eng.), 2nd Japan-Sweden Workshop on Advanced Spectroscopy of Organic Materials for Electronic Applications (Hayama, Japan), 21 - 25 October.

Grants

Asami K, Manipulation of Single Biological Cells by AC Fields and Their Dielectric Spectroscopy, Grant-in-Aid for Scientific Research (C)(2), 1 April 2002 - 31 March 2004.

Sato N, Development of Novel Electronic Systems Based on Hybridization of Characteristic Molecular Properties and Specific Aggregate Structures, Grant-in-Aid for Scientific Research (2) on Priority Areas of Molecular Conductors, 17 October 2003 - 31 March 2008.

Direct observation of electronic structures of unoccupied states in lithium phthalocyanine thin films in relation to their polymorphism

Lithium phthalocyanine (LiPc) is a neutral radical which is stable even in the air; it has an unpaired electron deriving a singly occupied molecular orbital (SOMO) according to its Pc macrocyclic ring, and then its physical properties, in particular, its intrinsic semiconductivity and magnetic behaviors, have attracted interests of many people in the research field of organic materials science. Besides, LiPc shows polymorphism as most Pc's do and the three different polymorphs, *i.e.* the x-, the α- and the β-forms, of crystals have been characterized so far by several research groups. Brinkmann *et al.* have reported that the x-form tetragonal crystal shows a notably low electric resistivity along the molecular stacking axis and that the monoclinic α-form one exhibits a Curie-Weiss susceptibility with a mean-field temperature characteristic of ferromagnetic couplings.

In this study, LiPc thin films in the x- and the α-forms were successfully prepared on gold substrates in the first place. Then their inverse photoemission (IPE) spectra were measured to examine any differences in the electronic structures of unoccupied states between two forms of the films, as the electronic structures of their valence states have been observed to be almost the same from a preliminary measurements of their ultraviolet photoemission spectra by Fujimoto *et al.* The obtained IPE spectra were interpreted with the aid of the results calculated for a LiPc molecule and its dimers in the forms corresponding to the x- and the α-forms using the density functional theory (DFT) method in collaboration with Sakaki *et al.*

The obtained IPE spectra for two kinds of the films were different from each other as shown in Fig. 1: the lowest energy feature originated from SOMO is located lower in energy for the α-form film, and the second lowest energy feature corresponding to the next lowest unoccupied molecular orbital (NLUMO) appears to be much broader for the x-form one. With referring to the obtained results from the calculations above, we have come to a conclusion on the spectral interpretation as follows: the broad feature for $6e_g$ orbital (NLUMO) for the x-form is understood by the removal of its degeneracy due to a large intermolecular interaction along the molecular stacking axis in the film, and the lower energy of $2a_{1u}$ orbital (SOMO) for the α-form is explained by higher contribution of electron correlation, both Coulomb and exchange repulsions, working in the x-form film in particular. On the basis of these conclusions, the different characteristics in the electrical and magnetic properties revealed between the x- and the α-forms of LiPc as mentioned above appear to be essentially elucidated to a large extent.

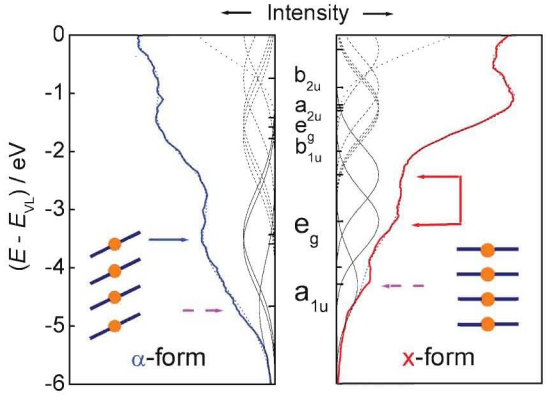

Fig. 1 Comparison of IPE spectra between the α-form and the x-form of LiPc films with respective molecular stacking manners shown schematically. The ordinate is the state energy with reference to the vacuum level and as for the abscissae spectral intensities increase toward both sides. The spectral deconvolution using Gaussian functions is shown for each datum with the assignments; the arrows point the energy positions of the notable spectral features. Inserted pictures exhibit molecular stacking manners schematically.

N-terminal insertion of alamethicin helices in voltage-activated ion-channel formation

Alamethicin, a 20-residue peptide, is supposed to form ion channels of a helix-bundle type by inserting the N-terminus into lipid bilayer membranes under sufficient voltages. In this study, the N-terminal insertion has been examined with an alamethicin dimer (di-alm) that is N-terminally linked by a disulfide bond. When di-alm was added to the *cis*-side membrane, it forms long lasting channels with the lifetime τ of about 100 ms at *cis*-positive voltages. The lifetime was reduced to a few milliseconds by addition of dithiothreitol (DTT) to the *cis*-side membrane, indicating that most of the channels were formed by the monomers (alm-SH) resulted from the cleavage of the disulfide bond in di-alm by DTT. The succeeding addition of tetrathionate (TT) to the *trans*-side produced channels of τ = 10-20 ms besides the channels of alm-SH. The results suggested that TT reacted with the N-terminal thiol group of alm-SH locating at the *trans*-side of the membrane to alter the lifetime. The N-terminal insertion of alamethicin helices by voltage activation, therefore, was confirmed.